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(54) Filter dyes for rapid processing applications.

(57) The synthesis and the application of new dyes is described, said new dyes being incorporated in non-migratory state in hydrophilic colloid layers of photographic materials wherefrom they can be rapidly removed after being quickly decolourized in alkaline aqueous liquids used in the processing of said materials. The filter dyes have an amide function or a derivative therefrom as a substituent at the mono- or trimethine chain.

EP 0 587 229 A2

1. Field of the invention.

The present invention relates to filter dyes and their use as antihalation and anti-cross-over dyes in photographic elements.

2. Background of the Invention

Non-spectrally sensitising dyes are widely used in photographic elements, particularly in photographic elements of the silver halide type. They may be used in a photosensitive silver halide emulsion layer as screening dyes, in an undercoat adjacent to the photosensitive layer and/or in a backing layer on the side of the support opposite to the photosensitive layer(s) to absorb reflected and scattered light thereby serving as antihalation dye or in an overcoat or interlayer to shield a particular photosensitive layer against undesired exposure being therefore referred to as filter or absorber dye, thereby adjusting the sensitivity of a photographic element as required in the production specifications.

For example in order to improve image sharpness an absorber dye can be present in one or more filter layers between silver halide emulsion layers that are coated at opposite sides of a transparent film support of an X-ray recording material. The imagewise exposure of said recording material proceeds in a cassette between a pair of X-ray intensifying screens that each are held in contact with an adjacent silver halide emulsion layer. By said arrangement the imaging light that would cross the support and to some extent becomes scattered thereby, is considerably attenuated and cannot give rise to an unsharp image in an opposite silver halide emulsion layer.

Spectrally the dye absorption spectrum should approximately be equal to the sensitivity spectrum of the corresponding silver halide emulsion in the layer of which a sharp image has to be reproduced.

On the one hand it is very important that filter dyes remain, i.e. that they are non-migratory, in the layer wherein they have been incorporated especially when this layer is in direct contact with the silver halide emulsion layer in order to prevent a desensitising action on the silver halide. On the other hand the filter dyes may not stain the photographic material after image processing. Therefore preference is given to filter dyes that decolorise or can be removed from the photographic element in the processing stage. This requirement is nowadays becoming more and more stringent as rapid processing times are of increasing interest.

As described in US-P 3,560,214 dyes comprising a carboxyl and phenyl substituted pyrazoline nucleus linked through a methine group to a dialkylaminophenyl group can be removed relatively easily in alkaline aqueous processing liquids but lack sufficient fastness to diffusion in hydrophilic colloid layers.

Other filter dyes characterized by the presence of a 2-pyrazolin-5-one nucleus substituted with a carboxyphenyl group and including a methine group or chain linked to a dialkylamino group are described in US-P 4,857,446. The decolorization of said filter dyes proceeds very rapidly in alkaline aqueous processing baths. The monomethine dyes have an absorption spectrum of which the maximum is in the shorter wavelength range of the visible spectrum so that normally a second filter dye is needed to block or absorb green light and even a third one to absorb radiations of longer wavelengths, e.g. radiations in the red or even in the infrared region.

Once a filter dye has been selected, the problem is how to get the filter dye in a coated layer so that all the requirements mentioned previously are met.

One of the possibilities is to make use of solid particle dispersions of water insoluble dyes as has been described in EP 0,384,633 A2; EP 0,323,729 A2; EP 0,274,723 B1, EP 0,276,566 B1, EP 0,351,593 A2 and US-Patents 4,900,653; 4,904,565; 4,949,654; 4,940,654; 4,948,717; 4,988,611 and 4,803,150.

Another possibility is offered in Research Disclosure 19551 (July 1980) which describes an approach of associating hydrofobic compounds with latex polymer particles.

EP 0,401,709 A2 describes the dissolution of hydrophobic dyes into oil droplets being substantially insoluble in water and the preparation of the corresponding oilformer dispersions or loaded polymer latex dispersions.

To prevent dye wandering, the dye is often coated with a mordant to bind the dye in the layer in which it is coated as is e.g. illustrated in US-Patent 2,527,583. As dye mordants polymers are often used.

Another possibility is offered by adsorption of dyes at the surface of very fine light-insensitive silver halide crystals with the expectable disadvantages of the coating of more silver halide crystals and possibly fixation difficulties.

Very few dyes satisfy the above requirements especially when rapid processing is concerned. Moreover, apart from the requirement of non-diffusibility and of rapid decolourizing or removal by rapid processing that the dyes should meet, they should have high stability in the photographic material, not only

under the influence of the ingredients present in the emulsion layers prior to coating, but especially under severe storage conditions of the packed material e.g. under circumstances of high temperatures and high degrees of humidity.

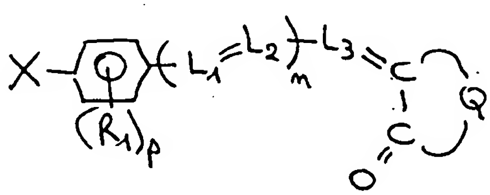
3. Objects and Summary of the Invention

It is an object of the present invention to provide new dyes that can be incorporated in non-migratory state in hydrophilic colloid layers of photographic materials wherefrom they can be rapidly removed in alkaline aqueous liquids used in the processing of said materials.

It is a further object of the invention to provide new dyes providing high density in the required spectral region, thereby reducing the cross-over effect in double-sided photographic elements, particularly radiographic materials.

Other objects will become apparent from the description hereinafter.

In accordance with the present invention dyes are provided corresponding to the following general formula (I):



(I)

wherein

n represents 0 or 1;

p represents 0, 1 or 2;

Q represents the atoms necessary to form an acidic nucleus such as pyrazolone, barbituric acid, thiobarbituric acid, rhodanine, hydantoine, oxazolidindione, thio-oxazolidindione, isoxazolinone etc.;

R_1 represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, $COOR_2$,$NHCOR_3$ or $NHSO_2R_4$ with R_2representing hydrogen or substituted or unsubstituted alkyl, R_3 and R_4 representing substituted or unsubstituted alkyl, or substituted or unsubstituted aryl;

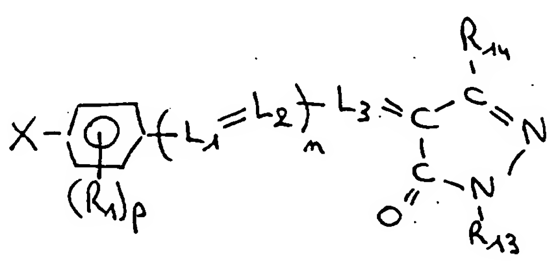
X represents OR_5, SR_5 or NR_6R_7 wherein

R_5 represents H, substituted or unsubstituted alkyl, substituted or unsubstituted aryl and each of R_6 and R_7 which may be the same or different represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl or the necessary atoms, e.g. trimethylene, to form a ring together with the N-atom to which they are attached and the C-atom of the phenylene ring in ortho position with respect to said N-atom; R_6 and R_7 together may also represent the necessary atoms to form a ring with the N-atom to which they are attached;

L_1, L_2, L_3 represent substituted or unsubstituted methine with the proviso that at least one of L_1, L_2 or L_3 must be substituted by - $CONR_8R_9$;

R_8 and R_9 which may be the same or different represent hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, NH_2, NHR_{10}, $NR_{11}R_{12}$ with R_{10}, R_{11} and R_{12} representing a substituted or unsubstituted alkyl, or a substituted or unsubstituted aryl and wherein at least one of R_1 to R_{12} contains an ionizable group.

More preferably dyes of the present invention correspond to formula (II):



(II)

wherein each of n, p, X, R_1, L_1, L_2 and L_3 has one of the meanings given hereinbefore and wherein R_{13} represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, or sulfolanyl, R_{14} represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, $COOR_2$, $NHCOR_3$, $NHSO_2R_4$, with R_2, R_3 and R_4 representing hydrogen, substituted or unsubstituted alkyl, or substituted or unsubstituted aryl, and wherein at least one of R_1 to R_{14} contains an alkali-soluble group.

In accordance with the present invention a photographic element is provided comprising a support and at least one photo-sensitive silver halide emulsion layer, wherein said element comprises, dispersed in a hydrophilic water-permeable colloid binder, e.g. gelatin, at least one dye according to the above general formula.

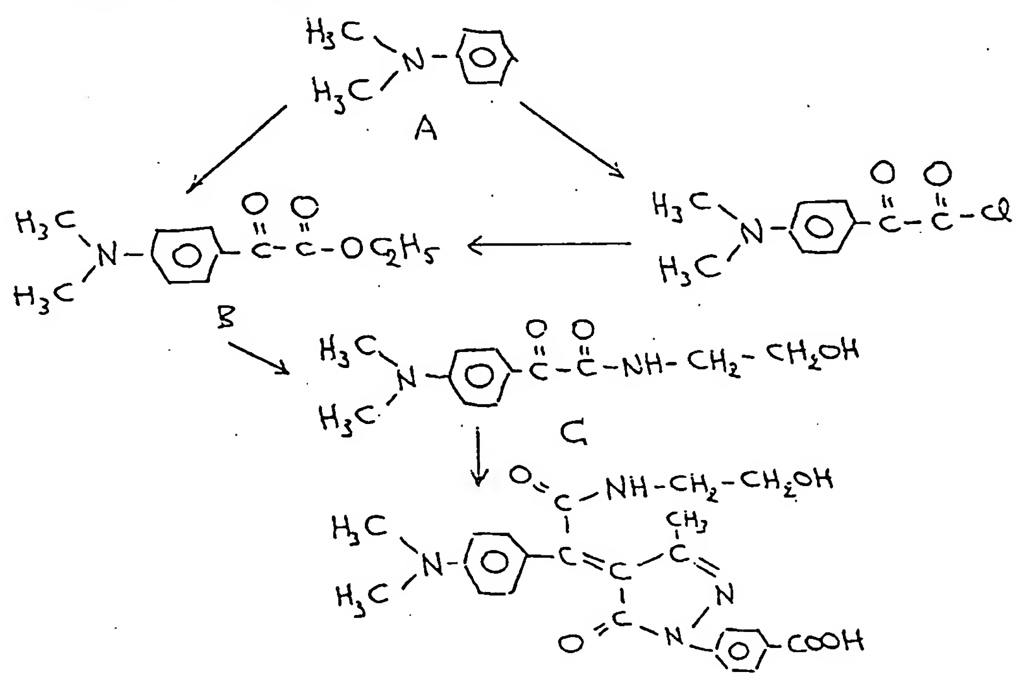
Further in accordance with the present invention a photographic element is provided comprising a support and at least one photo-sensitive silver halide emulsion layer, wherein said element comprises said at least one dye according to the above formula in a solid particle state by acidifying the slightly alkaline coating solution "in situ" at the moment the coating solution is applied.

4. Detailed description of the Invention

The presence of an amide group as a substituent on the methine chain is very characteristic for the dyes suitable for use in this invention.
The absence of this amide-group does not only affect the spectral behaviour, shifting the absorption to shorter wavelengths, but doesn't allow the dye to be decolourized quickly enough, as required in rapid processing conditions, especially for 38 s processing cycles.

The synthesis of dyes according to the present invention may follow different suitable ways, a schematic way of synthesizing said dye being illustrated in reaction scheme 1 given hereinafter.

Reaction scheme 1.



The monomethine dyes can be synthesized via different suitable ways.
One way consists in the conversion of dialkylaminobenzene A to the alpha-keto-ester B. At least three methods are described in literature:

a. The reaction of A with diethyl oxalate in the presence of aluminum trichloride (Guyot, Compt. Rend. 144, 1120 (1907)).

b. The reaction of A with oxalyl chloride, followed by ethanolysis of the intermediate acid chloride (Staudinger, Stockmann, Chem. Ber. 42, 224 (1909)).

c. The reaction of A with ethyl oxalyl chloride (Michler, Hanhardt, Chem. Ber. 10,2081(1877)).

The thus obtained ester B is then converted to the amide C by treatment with ethanolamine.

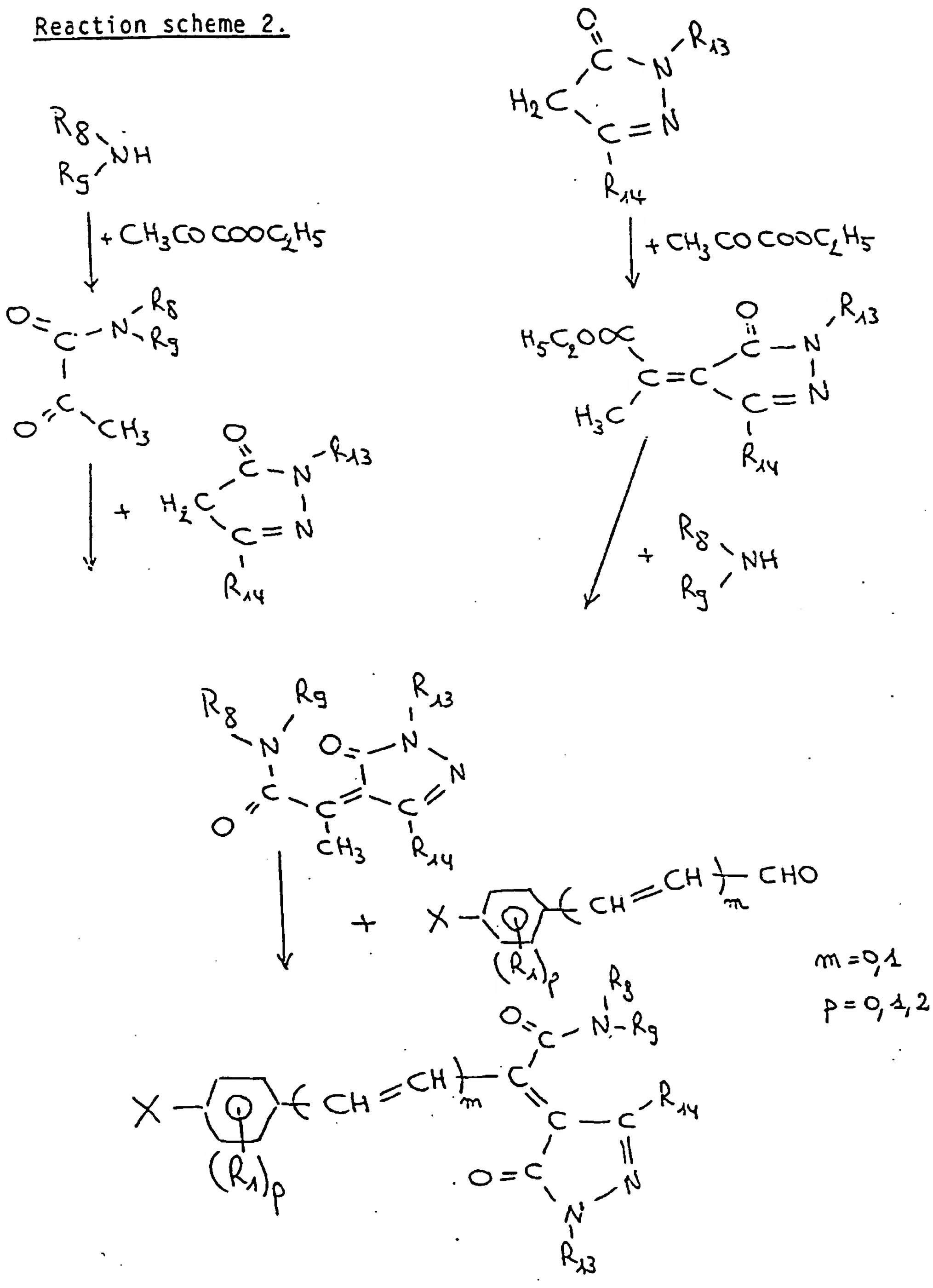
Following the second suitable way, amides such as C can be obtained directly by reaction of amines with the intermediate acid chloride as is described (but not for C) in Wright and Gutsell, J. Org. Chem. 24, 265 (1959).

Keto-amides such as C can easily be condensed with acidic nuclei such as pyrazolones by several known methods including refluxing the components in toluene with azeotropic destillation or refluxing the components in ethanol using known catalysts such as amines, amine salts or zinc chloride.

Dispersions of the dye obtained following reaction scheme 1 according to this invention show a maximum absorption peak at a wavelenght of 560 nm, said wavelength value being shifted about 100 nm more bathochromically in comparison with the corresponding dye without amide-substitution.

Trimethine (and even pentamethine) dyes may be obtained following reaction scheme 2 according to this invention.

Reaction scheme 2.



From the prior art it is known that the presence of one or more anionic, weakly-acidic groups in the dyes is important to provide sufficient non-migratory character at coating pH values in the range of 4 to 8.

In the acid pH range the filter dyes according to the present invention can be incorporated in aqueous coating compositions in dispersed form by using commercial mixing devices for making colloidal dispersions, e.g. in gelatin. The size of the dye particles obtained is chosen to facilitate coating and rapid decolouration of the dye. Where the dyes are initially crystallized in the form of particles larger than desired for use, conventional techniques for achieving smaller particle sizes can be employed, such as ball milling, roller milling, sand milling and the like. The solid particle dispersions cannot only be prepared in the presence of gelatin as a colloidal medium but also e.g. in colloidal silica. A preferred method of preparing

an aqueous solid particle dispersion of a photographically useful compound, for incorporation in one of the layers of a photographic silver halide material comprises the steps of

- dissolving a non-watersoluble but alkali-soluble compound in an aqueous alkaline solution, if necessary with the help of an organic water soluble solvent
- precipitating the said compound from said solution in the presence of colloidal silica sol, preferably in the further presence of a dispersing agent by lowering the pH of the solution, e.g. by neutralizing with an aqueous acidic solution
- removing water-soluble salts formed by the precipitation and any organic solvent used, and
- concentrating the dispersion either during or after the precipitation by dialysis or ultrafiltration or after precipitation by flocculation and decantation, followed by washing and further decantation.

Said precipitation in the presence of colloidal silica sol preferably occurs in the further presence of a dispersing agent, like e.g. a 2-N,N,N-trialkylamino-acetic acid and can be performed by simultaneous addition of an aqueous alkaline solution comprising the alkaline-soluble compound and an aqueous acidic solution, to a stirred solution comprising the total or partial amount of colloidal silica sol and of dispersing agent while keeping the pH constant, preferably at a value of less than 6.0, the rest of said amount if any being present in at least one of said solutions.

Preferred dispersing agents used during the preparation of solid silica dispersions are one or more partially ionizable polymer(s) or one or more surfactant(s) or a combination thereof.

Another possibility to obtain ultra fine dye dispersions consists in acidifying a slightly alkaline coating composition during the preparation of the coating composition or "in situ" just before coating it onto the supporting layer. It has been found that the application of this dosage technique allows us to obtain the dyes in a very fine solid particle form, homogeneously divided into the coated layer so that solid particles can hardly be observed even by means of microscopic techniques.

The non-diffusing dyes the synthesis of which has been described hereinbefore and which are added to a hydrophilic layer of a photographic element as a solid particle have a mean diameter of less than 10 μm, more preferably less than 1 μm and still more preferably less than 0.1 μm.

At a pH of at least 10 the dispersed filter dyes are easily solubilized so they are removed almost completely from a hydrophilic waterpermeable colloid layer of a photographic silver halide emulsion material by its common alkaline aqueous liquid processing and leave almost no residual stain. The presence of sulfite in the processing solution contributes to a more rapid discoloration of the filter dyes.

Particularly for 38 s processing cycles, comprising a development, fixing, rinsing and drying step, photographic elements with dyes according to this invention in one or more hydrophilic layers are very rapidly discoloured.

The hydrophilic colloidal layer(s) in which the dye(s) are incorporated in accordance with the present invention can be a backing layer, an antihalation undercoating layer, a silver halide emulsion layer, an intermediate layer and a protective outermost - layer.

Emulsion layers in accordance with this invention may contain light-sensitive silver halide crystals with a diameter of at least 0.1 μm. Intermediate layers in accordance with the present invention may contain very fine light-insensitive silver halide particles with a diameter of 10 to 100 nm known as Lippmann emulsions, incorporated into said layers e.g. to serve as scavangers to prevent oxidized developer products to migrate into adjacent layers.

The layers previously mentioned as suitable layers comprising a filter or antihalation dye may be incorporated in e.g. X-ray materials, graphic arts materials, diffusion transfer materials, black and white or colour cinematographic materials etc.

According to a preferred embodiment the dye or dyes are incorporated in a antihalation back coating layer for single-coated materials or a antihalation undercoating layer or layers, especially for double-coated materials as e.g. X-ray photographic materials.

In an outermost layer or layers or in an emulsion layer or layers one or more dyes according to this invention may be used to adjust the sensitivity of the photographic material as required by the production specifications. So it is possible to apply a dosing feeder just before coating the hydrophilic layer concerned and to control the production of the photographic material in this way, the dye(s) being present in the form of a gelatinous dispersion or in a solid particle state.

The dyes absorbing in the green spectral range being frequently used trimethine dyes can be used advantageously between silver halide emulsion layers of double-sided emulsion coated (duplitized) photographic film material applied in X-ray recording for use with green light emitting X-ray conversion phosphor screens. By said arrangement the green light that would cross the support and to some extent become scattered thereby, is considerably attenuated and cannot give rise to an unsharp image into an opposite silver halide emulsion layer.

Green light emitting phosphor screens and their use in combination with green sensitive silver halide emulsion layers of a double side coated (duplitized) film are described e.g. in US-P 4,130,428, wherein also several measures, e.g. the use of filter dyes, to reduce cross-over light have been described.

In a particular embodiment of the present invention the dyes are incorporated into a radiographic material that is provided at both sides of the support with a silver halide emulsion layer and an antistress layer as a protective layer coated thereover. The radiographic material preferably has on both sides of the film support silver halide emulsion coatings that are split into two distinctive emulsion layers having silver halide crystals of different average grain size one of which is a high speed emulsion layer and the other is a low speed emulsion layer; the high speed emulsion layer being situated at a larger distance from the support than the low speed emulsion layer. This way the sensitometric curve can be fine-tuned, giving the perfect profile for the specific application. The layer arrangement may also be opposite to the previously cited sequence in order to get a higher contrast. Moreover even without using a separate anticrossover layer this layer arrangement reduces crossover, especially in the critical low density area. In the presence of crossover preventing antihalation undercoat layers containing the dyes according to this invention the crossover reduction is improved without leaving a colour stain upon processing, especially upon rapid processing in less than 60 seconds, preferably in 38 seconds as a reference processing time of materials with high-throughput.

All combinations of symmetrically double-sized films with a symmetric or asymmetric set of intensifying screens or combinations of double-sized films with asymmetric emulsion layers, whether or not duplitized, in combination with a symmetric or asymmetric set of intensifying screens can be useful, depending on the specific needs required.

According to another embodiment said green-light absorbing dyes can be used in a antihalation layer of a photographic silver halide emulsion material in order to improve image sharpness by absorbing exposure light penetrating the emulsion layer(s) into the direction of the support. The use of said mainly green light absorbing dyes in an antihalation layer is particularly advantageous in silver halide emulsion materials that are made spectrally sensitive to green light and of which the exposure proceeds with a green light emitting laser e.g. argon ion laser the main power of which is emitted at 488 and 514 nm.

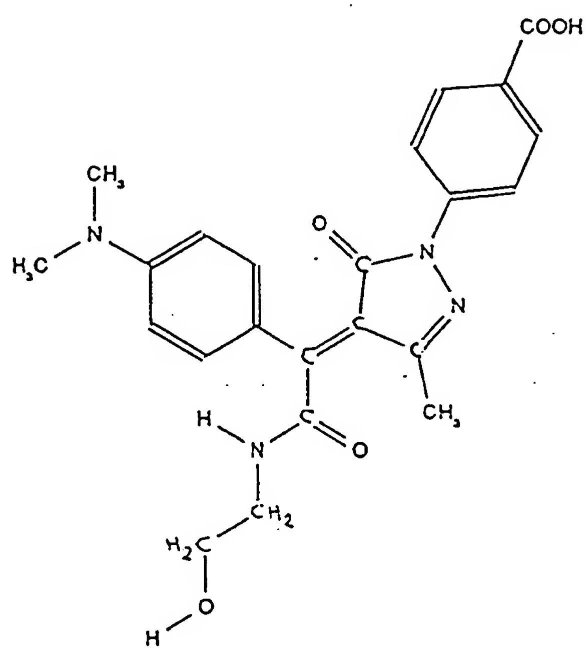
The following examples illustrate the present invention without however limiting it thereto.

EXAMPLES

In Table I, formulae of the dyes as used in the examples are given.

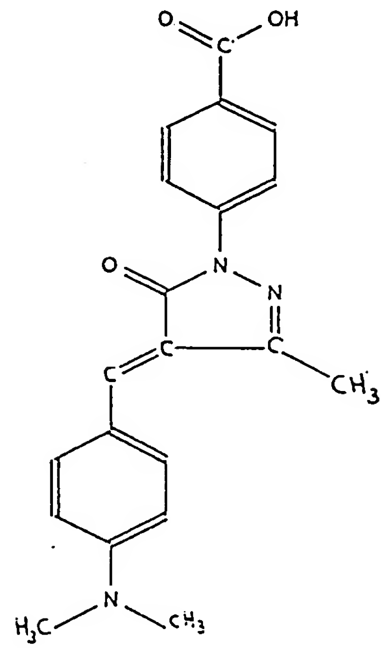
Table I: Formulae of the dyes used in the examples.

Dye 1 (invention)



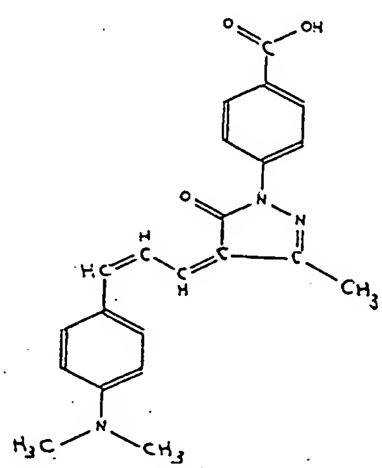
(I)

Dye 2 (comparative example 1, corresponding to Dye 1 of Table 1 of US-P 4,857,446)



(II)

Dye 3 (comparative example 2, corresponding to Dye 11 of Table 2 of US-P 4,857,446)



(III)

1. Synthesis of the monomethine dye 1.

89.4 ml of oxalyl chloride and 500 ml diethylether were placed in a reactor vessel and colled to 0 °C. A solution of N,N-diemthylaniline in 500 ml diethyl ether was carefully added over a period of 1 hr. The reaction mixture was stirred overnight at 0 °C, after which time 183 ml ethanolamine was added, followed by

a solution of 80 g NaOH in 1000 ml water. The yellow precipitate (193 g) was filtered and was shown to have an amide structure corresponding to formula B, given hereinbefore. 1.18 g of the amide, 1.09 g 1-(4-carboxyphenyl)-3-methyl pyrazolone and 1 g $ZnCl_2$ were refluxed in 25 ml ethanol for 24 hrs. The resulting red precipitate (1.9 g) was rinsed with acetone and dried, and was shown by spectroscopy to have the structure of product C (dye 1) given hereinbefore.

2. Optical properties of the dyes coated as a dispersion on a film support.

- Procedure for the preparation of the dye dispersion

  10 g of filter dye was dispersed at 40 °C in 200 g of a 10% aqueous gelatin solution by using a rotating pearl mill containing as a milling material zirconium oxide pearls sizing 0.6 to 0.8 µm. At a dye particle size of about 1 µm the milling process was stopped and the dispersion separated from the milling material.
- Coating procedure

  Chromium (III) acetate as a hardening agent and an additional amount of gelatin were added to the above prepared dye dispersion kept at a temperature of 36 °C and a pH value of 6.1.

  Said dispersion was double-side coated and dried on a polyethylene terephtalate film support of 175 µm thickness in order to obtain at each side a dye coverage of 0.1 g/m^2, a gelatin coverage of 1 g/m^2 and a coverage of hardening agent of 0.016 g/m^2.

In Table II the maximum absorption wavelength (λ-max) of the coated materials is given together with the half band width (HWB) values of the absorption wavelength expressed in nm, the density (D) measured at λ-max and at 540 nm, the latter being the main emission wavelenght of a Gd_2O_2S:Tb phosphor used in X-ray intensifying screens. Absorption spectra were measured at a Diano Corporation Match Scan spectrophotometer with diffuse light.

Table II

Optical properties of dyes in the coated layer.				
Dye No.	λ-max (nm)	HBW (nm)	D at λ-max	D at 540 nm
1 (invention)	560	166	0.41	0.40
2 (comparison)	455	176	0.43	0.24
3 (comparison)	500	231	0.63	0.60

In order to assess the resistance to diffusion of the dye in the coated layer, the above described coating of each dye was rinsed with destilled water at 20 °C for 5 minutes. Before and after rinsing the spectral density D at λ-max was measured at the double-side coated material as has been summarized in Table III.

Table III

Density measured at the maximum absorption wavelength λ-max.		
Dye No.	D at λ-max	
	Before rinsing	After rinsing
1 (invention)	0.41	0.40
2 (comparison)	0.43	0.43
3 (comparison)	0.63	0.62

The negligible change in spectral density D at λ-max before and after rinsing with water is a measure for the resistance to diffusion of the dye in the coating layer.

3. Decolourizing properties of the dyes, coated in an anti-crossover layer, under practical processing conditions.

To check the decolourizing properties of the dyes in practical circumstances the dyes were coated on both sides of a polyethylene terephtalate film support in an anti-cross-over layer and were overcoated with

an emulsion layer and a protective layer. The dye coverage was adjusted so that the optical density at 540 nm was 0.15 for the double side coated sample. Next, the samples were processed in a 90 or 38 seconds processing cycle and the spectral density at λ-max of the dye was determined. A low value of this spectral density means that the dye decolourizes well during the processing. The composition of the sample coatings, developer and fixers and the processing conditions are given hereinafter:

Composition of the coated samples.

In the emulsion layer no use was made of a spectral sensitizer because of the interference of its absorption spectrum with the dyes under investigation. The coating weight, expressed in g/m² per side of the different layers, was as follows:

- anti-cross-over layer:

gelatin	1g/m²
dye	see Table IV
chromium(III) acetate	0.016 g/m²

- emulsion layer: all amounts are given in g/m²

AgBr(I)-crystals (2 mole% of iodide; 98 mole% of bromide) (as $AgNO_3$)	4.15
gelatin	2.10
4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.006
sorbitol	0.20

- protective layer:

gelatin	1.10
polymethylmethacrylate (average particle diameter: 6 µm)	0.023
formaldehyde	0.10

Processing conditions and composition of developers.

- Conditions for the 90 seconds processing cycle.
- processing machine : CURIX 402 (Agfa-Gevaert trade name) with the following time (in seconds (sec.)) and temperature (in °C) characteristics:

loading	3.4 sec.
developing	23.4 sec./ 35 °C in developer AGFA G138 (trade name)
cross-over	3.8 sec.
fixing	15.7 sec./ 35 °C in fixer AGFA G334 (trade name)
cross-over	3.8 sec.
rinsing	15.7 sec./ 20 °C.
drying	32.2 sec. (cross-over time included)
total time	98.0 sec.

- Conditions for the 38 seconds processing cycle.
- processing machine : CURIX HT530 (Agfa-Gevaert trade name) with the following time (in seconds (sec.)) and temperature (in °C) characteristics:

loading	0.2 sec.
developing	9.3 sec./ 35 °C in developer II described hereinafter
cross-over	1.4 sec.
rinsing	0.9 sec.
cross-over	1.5 sec.
fixing	6.6 sec./ 35 °C in fixer II described hereinafter
cross-over	2.0 sec.
rinsing	4.4 sec.
cross-over	4.6 sec.
drying	6.7 sec.
total time	37.6 sec.

Composition of the three-part developer for the 38 seconds processing cycle

- concentrated part A

hydroquinone	106.0 g
potassium sulphite (65% solution)	249.0 g
potassium bromide	12.0 g
ethylenediamine tetraacetic acid, sodium salt trihydrate	9.6 g
potassium hydroxyde	77.0 g
potassium carbonate	38.0 g
sodiumtetraborate, decahydrate	70.0 g
5-methylbenzotriazole	0.076 g
diethylene glycol	56.0 g
demineralized water to make 1 liter pH adjusted to 11.80 at 25 °C with potassium hydroxide.	

- concentrated part B:

phenidone (1-phenyl-3-pyrazolidinone)	20.0 g
acetic acid	30.1 g
5-nitro-indazole	1.15 g
diethylene glycol to make 100 ml	

- concentrated part C:

glutaric dialdehyde 50% solution)	17.8 g
potassium metabisulphite	26.0 g
water to make 100 ml	

For initiation of the processing the three parts were mixed in the following ratio: 250 ml of part A, 700 ml of water, 25 ml of part B and 25 ml of part C. No starter solution was added. A pH of 10.40 at 25 °C was measured.

Composition of fixer II (containing a hardener)

- concentrated part A:

ammoniumthiosulphate (78% solution)	661 g
sodium sulphite	54 g
boric acid	25 g
sodium acetate trihydrate	70 g
acetic acid	40 g
water to make 1 liter	
pH adjusted with acetic acid to 5.30 at 25 °C.	

- concentrated part B:

water	150 ml
acetic acid	10 g
sulphuric acid	13 g
aluminium sulphate (34% solution)	27 g
water to make 250 ml	

The fixer ready for use was then made by mixing concentrated part A, water and concentrated part B in the following ratio: respectively 250 ml, 687.5 ml and 62.5 ml. A pH of this mixture of 4.25 at 25 °C was measured.

Densities at λ-max of the dyes after processing are given in Table IV.

Table IV: Evaluation of the optical densities of the dyes.

Dye No.	coated dye amount in g/m^2 per side	optical density at λ-max after processing 90 s cycle	38 s cycle
1 (invention)	0.038	0.000	0.020
2 (comparison)	0.063	0.000	0.015
3 (comparison)	0.025	0.005	0.025

As can be seen from Table IV, even in the 38 s-processing cycle the optical density at the maximum absorption wavelength is reduced to an acceptable level.

4. Evaluation of the photographic properties of the dyes in an anti-cross-over layer.

Coating procedure

The coatings of item 3 were repeated, except for the addition per mole of $AgNO_3$ used for the emulsion of 470 mg of the spectral sensitizer anhydro-5,5'-dichloro-3,3'-bis(n.sulfobutyl)-9-ethyloxacarbo-cyanine hydroxide. In addition a coating without a dye added to the anti-cross-over layer was performed as a reference.

Exposure,sensitometric and densitometric data:

Samples of those coatings were exposed with green light of 540 nm during 0.1 seconds using a continous wedge and were processed during the 90 seconds cycle described below. The density as a function of the light dose was measured and therefrom were determined the following parameters:

- fog level (with an accuracy of 0.001 density),
- the relative speed S at a density of 1 above fog (the sample with the comparative example was adjusted to a relative speed value of 100),

Determination of the cross-over percentage:

The cross-over percentage (% cross-over) was determined as follows. The double side coated samples were adjusted between a single green light emitting screen (CURIX ortho Regular : Agfa-Gevaert trade name) and a white paper, replacing the second screen. This film-screen element, directed with its light emitting screen to the X-ray tube, was then exposed with varying X-ray doses, expressed as log E. After processing these samples in the 90 seconds cycle, the minimal dose (log E) needed to obtain a density of 0.5 above fog was determined for the frontlayer (log E front) and the backlayer (log E back) separately. The cross-over percentage was then calculated according to the following equation :

% cross-over = 100/antilog(logE back - logE front)

In table V the results of these photographic tests are tabulated.

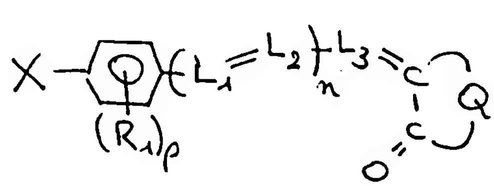
Table V

Photographic effect of the dyes in an anti-cross-over layer: sensitometry and cross-over percentage.				
sample Dye No.	coated dye amount per side(g/m²)	fog	sensitometry	
			speed	% cross-over
no dye (reference)	0	0.016	100	40
dye 1 (invention)	0.038	0.017	83	30
dye 2 (comparison)	0.063	0.017	89	31
dye 3 (comparison)	0.025	0.017	83	28

This table shows that the dyes (invention and comparative examples) significantly reduce the cross-over percentage with an acceptable decrease in sensitivity. It is further shown that fog is not influenced in the presence of the dyes, and that even with a significantly lower coating weight, the dye according to the invention shows a similar crossover percentage as dye 2-used in the comparative coating. Besides even versus dye 3, which is coated in a-lower amount and which shows similar sensitometric results and cross-over characteristics, the decolourizing properties are better for the dye in accordance with this invention, especially for shorter processing cycles, e.g. the 38 s cycle, as has been shown in Table IV hereinbefore.

Claims

1. A photographic material comprising a support and at least one light-sensitive silver halide emulsion layer characterised in that it comprises in a hydrophilic colloid layer at least one filter dye corresponding to the following general formula (I):

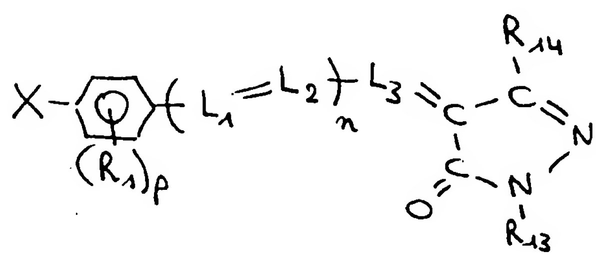


(I)

wherein

n represents 0 or 1;
p represents 0, 1 or 2;
Q represents the atoms necessary to form an acidic nucleus such as pyrazolone, barbituric acid, thiobarbituric acid, rhodanine, hydantoine, oxazolidindione, thio-oxazolidindione, isoxazolinone etc.;
R_1 represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, $COOR_2$,$NHCOR_3$ or $NHSO_2R_4$ with R_2 representing hydrogen or substituted or unsubstituted alkyl, R_3 and R_4 representing substituted or unsubstituted alkyl, or substituted or unsubstituted aryl,
X represents OR_5, SR_5 or NR_6R_7, wherein
R_5 represents H, substituted or unsubstituted alkyl, substituted or unsubstituted aryl and each of R_6 and R_7 which may be the same or different represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl or the necessary atoms, e.g. trimethylene, to form a ring together with the N-atom to which they are attached and the C-atom of the phenylene ring in ortho position with respect to said N-atom; R_6 and R_7 together may also represent the necessary atoms to form a ring with the N-atom to which they are attached;
L_1, L_2, L_3 represent substituted or unsubstituted methine with the proviso that at least one of L_1, L_2 or L_3 must be substituted by - $CONR_8R_9$;
R_8 and R_9 which may be the same or different represent hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, NH_2, NHR_{10}, $NR_{11}R_{12}$ with R_{10}, R_{11} and R_{12} representing a substituted or unsubstituted alkyl, or a substituted or unsubstituted aryl
and wherein at least one of R_1 to R_{12} contains an ionizable group.

2. A photographic material according to claim 1 wherein said at least one dye is a filter dye corresponding to the following general formula (II):



(II)

wherein each of n, p, X, R_1, L1, L_2 and L_3 has one of the meanings given in claim 2 and wherein
R_{13} represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, or sulfolanyl,
R_{14} represents hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl,$COOR_2$, $NHCOR_3$, $NHSO_2R_4$, with R_2, R_3 and R_4 representing hydrogen, substituted or unsubstituted alkyl, or substituted or unsubstituted aryl, and wherein at least one of R_1 to R_{14} contains an alkali-soluble group.

3. A photographic material according to any of claims 1 or 2 wherein said at least one filter dye is incorporated into an antihalation undercoat layer coated between the support and at least one silver halide emulsion layer.

4. A photographic material according to any of claims 1 or 2 wherein said at least one filter dye is incorporated into a backing layer.

5. A photographic material according to any of claims 1 to 4 wherein the dye(s) is (are) present in a hydrophilic colloid layer in an amount of 0.01 to 1.0 mmole/m^2.

6. A photographic material according to any of claims 3 to 5 wherein the filter dye(s) is (are) present as a gelatinous dispersion(s).

7. A photographic material according to any of claims 3 to 5 wherein the the filter dye(s) is (are) present as solid silica particle dispersion(s).

8. A photographic material according to any of claims 3 to 7 wherein said photographic material is an X-ray material.

9. Use of a photographic material according to claim 8 for rapid processing applications shorter than 60 seconds, comprising the developing, fixing, rinsing and drying steps.